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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 4 : G01N 33/00 — A1

(11) International Publication Number: WO 87/ 01204

(43) International Publication Date: 26 February 1987 (26.02.87)

(21) International Application Number: PCT/US86/01625

(22) International Filing Date: 6 August 1986 (06.08.86)

(31) Priority Application Number: 766,022

(32) Priority Date: 15 August 1985 (15.08.85)

(33) Priority Country: US

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(81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent).

**Published**
*With international search report.*

(54) Title: CHEMICAL ANALYSIS BY CONTROLLED SAMPLE MODULATION AND DETECTION CORRELATION

(57) Abstract

A method and apparatus for chemical analysis of a continuous gas stream for components of the stream that are not usually separately detectable. The method involves modulating a characteristic of one or more of the components of the stream in a predetermined and controlled manner, then detecting a signal representative of the gas stream containing the component with the modulated characteristic, and then correlating the detected signal with the predetermined and controlled modulation of the characteristic of the component in the stream to produce a correlation response to identify the presence and to quantify the modulated component within the continuous stream. One or more components may be identified and quantified by the method. The method has particular use in identifying methanol and hydrocarbons in the exhaust gases of a vehicle operated on a fuel containing methanol and hydrocarbons.

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# CHEMICAL ANALYSIS BY CONTROLLED SAMPLE MODULATION AND DETECTION CORRELATION

## FIELD OF THE INVENTION

This invention relates to a method and apparatus for differentiating between two or more chemical components or classes of chemical components in a gaseous mixture and more particularly to a method and apparatus for controlled modulation of a characteristic of at least one of two or more components to be differentiated, then detecting the presence of the one or more components with a suitable detecting means, and differentiating among the components by correlating the detected signal with the controlled modulation to identify the component or components that were to be identified. The method and apparatus has particular application to the identification and differentiation of components in mixtures of gaseous components in a continuous stream of the mixture and where individual gases within the mixture are not easily distinguishable by a single detection process.

## BACKGROUND OF THE INVENTION

For a variety of reasons it has become desirable to know the composition of continuously flowing gas streams comprising a mixture of components and to know the composition in a rapid manner. Prior art systems for determining composition of such a stream have usually required collecting a sample of the gas stream and then treating the sample in a batch analysis system such as by chromatography. Such a batch system is time consuming and only as accurate as the sensitivity of the detecting process within the system for each component of the stream. Conventional chromatography is not effective on a continuous stream because the components of the stream, even if seperated, become remixed in the continuing stream of carrier gas. Chromatography can be a valuable means for identifying components in the continuous stream if there were a way to seperate and identify the individual components of the stream as they passed through the detector of the chromatograph. The present invention proposes a method and apparatus for

accomplishing such a seperation and identification.

A series of publications by one of the present inventors, John B. Phillips, with other authors, have described a method for operating a chromatograph that is expected to improve the sensitivity of the chromatographic process. These papers include:

1. MULTIPLEX GAS CHROMATOGRAPHY, John B. Phillips, ANALYTICAL CHENISTRY, VOL. 52, NO. 4, April 1980
2. CONCENTRATION MODULATION BY THERMAL DECOMPOSITION FOR MULTIPLEX GAS CHROMATOGRAPHY, J.R.Valentin, C.G.Carie and J.B.Phillips, JOURNAL OF HIGH RESOLUTION CHROMATOGRAPHY & CHROMATOGRAPHY COMMUNICATIONS, Vol. 6, November 1983
3. DETERMINATION OF METHANE IN AMBIENT AIR BY MULTIPLEX GAS CHROMATOGRAPHY, Jose R. Valentin, Glenn C. Carle, and John B. Phillips, ANALYTICAL CHENISTRY, Vol 57, No. 6, May 1985
4. THERMAL MODULATION BOOSTS GC SENSIVITY, January 14, 1985 C&EN, Page 62

In these papers the authors have described techniques for operating a chromatograph to improve its sensivity. These improved techniques are applied to the present invention for the purpose of identifying a distinguishing characteristic of at least one substance in the presence of another substance in a continuously flowing stream.

In accord with the present invention a continuous stream containing components of at least two substances to be distinguished is passed through a continuous processing system wherein a characteristic of at least one of the substances is modulated with respect to others of the components in the stream and the presence of the component is detected within the system in a manner that responds to the modulation of the characteristic. The modulation of the characteristic is done in a predetermined manner and the detected response is compared to the predetermined modulation in a manner to correlate the

response with the modulation to identify the component subject to the controlled modulation. In this modulation, detection and correlation process the sensitivity of the system is enhanced and the presence of otherwise indistinguishable components may be identified.

## SUMMARY OF THE INVENTION

The present invention is a system and apparatus that will permit the identification and at least relative quantification of components of a continuously flowing stream of a mixture of components. The invention has particular application to the analysis of vehicle exhaust gases and is useful in the analysis of exhaust gases from vehicles operating on fuels that contain methanol. Prior art methods for the analysis of such gases have been slow and inaccurate because the detection of methanol and hydrocarbons in the presence of each other in a gas mixture can not be accomplished with generally the same techniques or processes. As here proposed and described the exhaust gases in a continuous stream are passed to a detector through a modulator that effects a characteristic of at least one of the gases of the stream in a manner that can be detected by the response of the detector. The modulation at the modulator and the response at the detector are then cross-correlated to produce a correlation signal which represents the presence or quantification of the component of the gas stream that was modified in the modulation process. If the gases of the mixed stream respond differently to the modulation process, the response of the detector will vary in accord with that difference in modulation and the correlation of the response to the modulation will produce a correlation signal that can identify and distinguish the different gases of the mixture.

The object of the present invention is a method and apparatus that may be used to identify and distinguish components of a mixture.

A further object of the present invention in accord with

the foregoing object is a method and apparatus that will permit the identification of at least one substance in the presence of another substance by a process that modulates a characteristic of one of the substances in a detectable manner and the detection of a response that may be correlated with the modulation to identify the one substance in the presence of the other.

In accord with the preceeding object the present invention contemplates physical and chemical modulations of the one substance as a means for producing a detector response that may be correlated with the modulation process to identify the presence of the one substance.

Further objects and features of the present invention will be readily apparent to those skilled in the art from the appended drawings and specification illustrating preferred embodiments wherein:

## BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic block diagram illustration of the process and elements used in the performance of the present invention.

FIG. 2 is a block diagram of a form of apparatus useful in modulating a sample stream in the performance of the present invention.

FIG. 3 is a block diagram of another form of apparatus useful in modulating a sample stream in accord with the present invention.

FIG. 4 is a block diagram of the process of the present invention as used in the analysis of automotive vehicle exhaust gases.

FIG. 5 is a block diagram of an apparatus capable of performing all of the steps of the method of the present

invention in the analysis of a sample substance.

FIG. 6 is a representation of an output correlation response that might be produced in performing the method of the present invention.

## DESCRIPTION OF PREFERRED EMBODIMENTS

The method and apparatus of the present invention comprises a system for differentiating between two or more chemical components or classes of chemical components in a gaseous mixture. In the drawings of this application the double lines between blocks are intended to illustrate passages for the flow of the gaseous mixture while the dotted lines are intended to illustrate operating control or signal channels and solid lines are energization connections. The invention includes four parts as shown in the block diagram of FIG. 1 where a gas mixture to be analyzed, as represented by the sample 10, is passed as a continuous stream through a modulator 12 where a characteristic, such as the gaseous concentration, of a component or component class of interest is intermittently modulated to an extent differing from the modulation of a characteristic of other components of the sample stream. The gas mixture with the component or components having modulated characteristics is then passed from the modulator to a transducer or detector 14 causing the generation of a response whose magnitude varies according to the concentration of the components in the gas stream.

FIG. 1 shows a filter 16 in phantom lines between the modulator 12 and the transducer 14 to indicate that such an element may be used as a part of the process but that the filter is not essential to the basic method.

A signal source 18 is operationally connected to the modulator 12 to control the operation of the modulator in a predetermined manner or controlled sequence. The control of the modulator in that manner causes a series of changes or

modifications of the characteristics in the gas stream that subsequently lead to corresponding changes in the output response or signal of the transducer 14. The output response of the transducer 14 is fed to a correlator 20. The correlator 20 is operationally interconnected with the signal source 18 so as to receive a representation of the modulating operation or control sequence of the modulator 12. As illustrated, a representation of the correlation produced in the correlator 20 is supplied as an input signal to a display or recorder at 22.

In accord with the present invention, the apparatus of FIG. 1 is capable of modulating a characteristic of at least a component of the gaseous sample by a modulator 12 controlled in a predetermined manner by a signal source 18 in a manner that will be detectable in the transducer 14 and the transducer response is fed to a correlator 20 along with the signal from the signal source for the purpose of producing an output signal that will represent the presence of the component that was to be identified in accord with the correlation of the detected response to the controlled modulation.

The modulator 12 will be designed to accomplish a desired modification or modulation of a particular component or components of the sample stream and the transducer will respond with an output response related to the presence of the particular conponent or components of the sample stream. The transducer responds to the concentration of the components passing through it and its output response is modulated according to modulation of the components of the sample stream produced in the modulator. The "raw" response signal represents the transducer's response to all the components in the gas stream and as such is not a response to single elements of the stream. However, when the response signal is correlated with the modulation signal, the correlation response will represent the effect of the modulator on the characteristics of a particular component or components of the sample stream in accord with the specific design or control of the modulator.

The system may be calibrated for components of interest by seperate repetition of the above described process, in which the gas mixture to be analyzed is replaced by a gas mixture containing one or more specific components in known concentration. The calibration process may be repeated with additional calibration mixtures of various known concentrations to develop a calibration curve that permits the sample gas mixture concentration to be determined by interpolation or like process.

The correlator output signal to the display 22 may be displayed or recorded in various forms, and converted by computation to units of concentration for the components in the gas mixture.

The filter unit 16 illustrated in the diagram may be useful for certain types of mixtures when it may be desirable to remove or alter certain chemical components or signals carried by such components that could produce signals at the transducer. Use of a filter can result in greater specificity or precision in the correlation process at the correlator 20. The filter may take many forms in both chemical and physical senses.

DESCRIPTION OF COMPONENT PARTS

The modulator may take many forms that will be effective to modulate a chemical characteristic of a component passing through it. It may be:

-a short bed of granular solids that is capable of absorbing, oxidizing, reducing, complexing, or otherwise removing or altering components from the sample gas mixture;

-an open coated tube having the same type of capabilities as above;

-an uncoated tube in which an electric spark can be induced;

-a tube through which ultraviolet or other radiation that produces chemical changes can be transmitted;

-and other devices capable of preferentially removing

specific chemical compounds from the flowing gas mixture.

FIG. 2 and 3 illustrate examples of systems with thermal and with catalytic modulators. In FIG. 2 the sample stream passes through a thermal modulator 24 formed by placing a conductive coating 26 around a portion of a chromatograph column 28. The thermal coating is energized from a power supply through a switch 32; the switch 32 is controlled by a microprocessor 34 to cause modulation of the desired characteristic of the sample stream. As in the basic system of FIG. 1 the gas stream passes through a detector 36, and signals from the detector and the microprocessor are supplied to a correlator 38 to produce the desired correlation signal. In FIG. 3 the sample steam is seperated into two portions. One portion of the sample stream passes to a detector 40 through a valve 42 and a catalyst tube 44 collectively functioning as a modulator. The other portion of the sample stream passes directly to the detector 40 through a valve 46. The catalyst tube 44 continuously modulates a characteristic of the components passing through it while the valve adds a time related control. The valves 42 and 46 are two way valves operating to pass the sample stream to the detector 40 or to discard or waste in accord with a predetermined manner prescribed by a microprocessor 48. As with FIG. 1 and 2 the output response of the detector 40 and the control signal of the microprocessor 48 are supplied to a correlator, not shown, to produce the desired correlation signal.

The operation of the modulator may be a reversible or an irreversible process, and in the irreversible case the modulation may be the destruction or chemical transformation of a particular component of the gas stream. The modulator accomplishes its modulation by interrupting the above operations, using heating, cooling, intermittent sparking or illumination, or other means dependent on the type of modulator. Some examples of thermal modulators are:

-a bed of chromatographic abdorbent whose activity is

enhanced by cooling;

-a bed of oxidation or reduction catalyst whose activity is enhanced by heating;

-and a chemical complexing agent whose activity is enhanced by cooling.

There may be one or more modulators in series, each being the same or different, with different thermal histories or of different types.

Possible granular solids for a modulator include calcium chloride and cobolt chloride.

The transducer or detector 14 may be any device that is capable of giving an electrical signal representative of the components of interest in the gas mixture that differs from that of the mixture not containing those components. There are many classes of detectors used in the practice of gas analysis and particularly in gas chromatography from which a suitable type may be selected for the particular application of interest. Examples are:

-FID (flame ionization detector), useful for hydrocarbons and most organics containing carbon;

- TCD (thermal conductivity detector), a general detector;

- ECD (electron capture detector), useful for compounds containing electronegative elements such as halogen atoms;

- and PID (photoionization detector), which is based on the ionization potential of the compound and is useful for aromatic compounds.

One or more of these may be used in series or in parallel.

In the signal source 18, electrical signals are generated in a selected sequence and used to initiate changes in the activity level of the chemical modulator 12. This causes chemical changes in the gas mixture, i.e. chemical signals, that are then detected at the transducer 14 and converted back to electrical signals there. The modulator signals are

intermittent pulses that may be generated by a computer, a microprocessor, a tape recorder, a strobe light, or even by a mechanical device analogous to a rotary switch. The intermittent pulses are not necessarily at uniform time intervals or of uniform duration. They actuate the modulator 12 by switching on a heater; by opening a solenoid valve to supply cooling gas; by initiating an electrical spark; by opening or closing a lamp shutter; or by other analogous means appropriate to the type of modulator. The sequence of actuation of the modulator is retained for use in the correlation process.

The central part of the system is the correlator 20 that correlates the modulator signal from signal source 18 with the signal from transducer 14 to produce the information desired, the concentration of the component or class of interest. The known sequence of modulator signals and the measured response signals of the detector are treated to seperate the signals due to that component or class from the other extraneous signals from the detector. In the simplest case this may involve little more than subtracting the modulator signal from the detector signal, after appropriate scaling or shaping. More elaborate means are cross-correlation or Fourier transformation. Both are mathematical techniques for extracting the information carried by the substance that was modulated from the transducer signal noise caused by non-modulated substances. The correlation process may produce a positive or megative signal response as the effect of the modulation on the sample substance is detected in the detector and correlated with the modulation process.

## EXAMPLES OF SPECIFIC APPLICATIONS

### Methanol in Vehicle Exhaust Gas

In exhaust from vehicles driven on mixtures of methanol and gasoline there may be unburned residues of both substances. In testing for such emissions it is desirable to differentiate between the two. In this case the sample gas mixture is exhaust gas diluted with air, and the component of interest is methanol. The four parts of the invention for performing this

differentiation are illustrated in block form in FIG. 4 where exhaust gas from an exhaust manifold 50 passes through a solenoid switch 52 to operate as an OFF/ON valve for the system. The exhaust gas then passes to a short thermal modulator 54 which may be in the form of a tube with a surface heater and containing a bed of solid adsorbant, a complexing agent, or an oxidation catalyst having greater activity toward methanol than hydrocarbon. A detector 56 in this system is shown as a flame ionization detector. The thermal modulator 54 is energized by power supply 58 through switch 60 under the control of a microprocessor 62. The response signal from the detector 56 and the control signal from the microprocessor 62 are supplied to the correlator 64 where the desired correlation signal is produced.

Alcohols, Aldehydes, and Carboxylic Acids in Vehicle Exhaust Gas

Besides the methanol fuel described in the preceeding paragraph, other alcohols are used as vehicle fuels or fuel additives, and products of partial combustion of these differ from those from hydrocarbon fuels. Methanol combustion, for example, may lead to production of formaldehyde, a toxic material. The configuration of the present invention for determination of these types of components, using the apparatus of FIG. 1, will be a modulator 12 suitable for the chemical class of interest, for example an oxidation catalyst for aldehydes (which are readily oxidized); a transducer 14 such as a FID or TCD; a signal source 18; and the correlator 20. In addition to these, there may need to be a filter in the form of a simple gas chromatographic column of a type suitable for the seperation of the chemical class of interest into its individual components. Identifying these classes of components may require a somewhat higher complexity in the correlation process and a more elaborate output system, because of the greater number of individual compounds, than for the methanol in vehicle exhaust system previously described. The effect of the delay in components moving to the detector because of seperation in the chromatographic column will be an element of the correlation process within the correlator.

Methane in Air

Methane is the principal component of natural gas. Knowledge of its concentration in air is important either as an indication of sub-surface gas generation (natural seeps or landfill generation) or of leaks in industrial distribution systems. In this determination the main constituent is air and there are often other hydrocarbons (heavier than methane) present. The four parts of the invention for performing this determination consist of a modulator 12, preferrably of the thermal type with an oxidation catalyst or an adsorbent (methane is unique among hydrocarbons in its oxidation and absorption properties); a transducer 14 of a suitable type such as FID or TCD; a signal source 18 and a microprocessor similar to that described for the methanol system.

Individual Low Molecular Weight Hydrocarbons in a Gas Mixture

This determination is useful in wellhead vapor analysis, leak detection , air pollution monitoring, and for process gases. The sample may be in air. As shown in FIG. 5, the invention's component parts are a thermal modulator 70 consisting of a short segment of a capillary quartz chromatographic column coated with electrically conductive paint; a detector or transducer 72 in the form of either a FID or a TCD (both are effective and each has advantages for particular applications); a microprocessor 74 providing signal pulses to switch power from a D.C. power supply 76 to the heater coating in the thermal modulator; and a correlator, in this form probably within the microprocessor, for demodulating the signals for the various hydrocarbons by cross-correlation with the signal pulses to the thermal modulator.

As in the other examples of the use of this invention, the sample flows through the system continuously passing here through a filter 78, a pump 80, a switching valve 82, a control valve 84, and a pressure gauge 86 in its route to the thermal modulator 70. The thermal modulator is connected to the detector 72 through a column 90. A source of calibration gas 88 is provided as an alternate input to the switching valve 82 to

provide for a calibration run through the system.

The thermal modulator 70, the detector 72, and the column 90 are enclosed within insulating barriers 92, 94 and 96, respectively, to provide for maintainence and control of the heat within those barriers. For the purpose of this system, the volume surrounding the thermal modulator would be maintained at ambient temperature, the volume around the columns would be maintained at about 50 degrees centigrade, and the volume around the detector at between 60 to 100 degrees centigrade.

Volatile Chlorinated Hydrocarbons

Because some of the components of chlorinated hydrocarbons are toxic, there is great interest in monitoring their concentration in the environment. A specific application of the present invention is the monitoring of air at waste disposal sited for emissions of this type of vapors. For this application, the system comprises a modulator making use of the affinity of certain metals such as silver for chlorine atoms, modulated by temperature pulsing; a detector probably of the TID type, which may be operated in a halogen mode; and a microprocessor for pulse control and demodulation by cross-correlation or other methods. A chemical filter or simple elementary gas chromatographic column in the input stages will be helpful.

Aromatic Hydrocarbons in Vehicle Exhaust

A system operated according to the present invention for this measurement would be simpler that the previous description of a system for measuring low molecular weight hydrocarbons. It could be made in two versions, one aimed at determination of benzene only, and another to determine also the higher homologs of benzene. The difference between this system and the system for identifying aromatics would be the use of a PID transducer, which can be made more specific for aromatic hydrocarbons relative to other hydrocarbons. Generally, all other elements would be the same. If the system was to be used for benzene detection only, the filter and the cross-correlator would be

even more simplified to give shorter initial delays in response.

Volitile Sulfur Compounds in Air or Natural Gas

Hydrogen sulfide and other organic sulfide and thiols in air are toxic nuisances. Certain thiols and sulfides are also used in various combinations as trace additives in natural gas and liquefied petroleun gas to give warning of leaks. The present invention may be used to monitor air concentrations or to analyze fuel gases for the concentrations of these compounds. For air sampling the system to perform the invention would comprise a modulator, probably based on the affinity of certain metals such as cadmium for sulfur; a transducer specific for sulfur, probably a flame photometric detector (FPD); a microprocessor for modulator control and demodulation such as by cross-correlation; and a chemical filter consisting of a simple gas chromatographic column designed for separation of the volitle sulfur compounds. For analysis of fuel gases the detector will require modification because of the totally combustible nature of the gas mixture. A supplemental supply of hydrogen gas to the detector will probably be necessary for either application.

## CORRELATION DISPLAY

The output may be displayed in the form of a digital output of concentration of the particular components detected or, if the filter is a chromatography column, a conventional gas chromatogram as shown in FIG. 6. Note that the chromatogram, because it is derived from the correlation of modulated and detected signals, includes both positive and negative signal representations. For example, as the modulator modulates an identifiable characteristic of a sample component by retarding and releasing a sample component in accord with the modulator's predetermined control, that modulation is detectable as the detector responds to all components within the sample stream. When the detector response signal is correlated with the predetermined control of the modulation process, the retarding and releasing may result in sequential positive and negative (or

reverse) correlation signals for identifying substances or components. The microprocessor can also be used for computations such as the BTU content (heating value) of the gas mixture or other desired computations.

## ADVANTAGES OF THE PRESENT INVENTION

The invention described in the foregoing will provide analytical information analogous to that obtained from gas chromatography, with the following advantages:

In the conventional gas chromatography the sample is introduced as a batch or slug of gas (sometimes by vaporization of a liquid in the inlet of the instrument). The sample is them passed through a column with adsorption properties, where the components of the gas mixture are separated and then detected individually as they emerge at the far end of the column. For the present invention the sample gas mixture is introduced continuously to the instrument, eliminating the need for manual or automated operation of valves (or syringe injection of liquids).

For applications not requiring the use of a chemical filter, this invention gives responses in a few seconds at most, and with a filter the results are read out at intervals of as small as one second, after an initial delay A filter can impose an initial delay of a few seconds to a few minutes; the longer delay results from a filter which is a chromatographic column. By contrast, the conventional gas chromatograph requires the same lag of seconds to minutes after each sample introduction.

The present invention also offers greater sensitivity because the sample is continuous;i.e. without overloading the system, more information (total sample) is used to calculate the result.

There is also the effect of the repetitive modulator pulsing, which has an effect analogous to repetitive sampling in

conventional gas chromatography, giving increased precision and lower detection limits in the same time interval.

There are minimum moving parts; a pump to introducing sample, a valve to switch to the calibration mixture, and in some cases valves to control auxiliary gases needed for the detector.

While certain preferred embodiments of the invention have been specifically disclosed, it should be understood that the invention is not limited thereto as many variations will be readily apparent to those skilled in the art and the invention is to be given its broadest possible interpertation within the terms of the following claims.

WE CLAIM:

1. A method for identifying a distinguishing characteristic of at least one substance in the presence of another substance in a continuously flowing stream including both of said substances, said one substance and other substance being in the same chemical phase, comprising the steps of:

a) passing at least a portion of said continuously flowing stream through a modulator means capable of modulating an identifiable characteristic of said at least one substance to modify said characteristic of said at least one substance with respect to at least said other substance in said portion of said stream;

b) passing said portion of said continuously flowing stream containing said one substance having said modulated identifiable characteristic through a detecting means capable of responding to said characteristic to produce a response signal;

c) controlling the operation of said modulator means in a predetermined manner to produce variations in said modulation of said identifiable characteristic of said at least one substance in accord with said predetermined control;

d) and comparing said produced response signal with said predetermined control of said modulator means to identify said one substance in said flowing stream by identifying variations in said response signal corresponding with said control of said modulator means.

2. The method of Claim 1 for identifying two different chemical substances in a mixture of at least those two substances in said continuously flowing stream, wherein said modulator means is capable of modifying a characteristic of at least one of said two substances, and said at least one chemical substance in said continuously flowing stream is identified from a correlation representation of modifications of said detected signal produced from comparing said signal of said detecting means with said control of said modulator means.

3. The method of Claim 1 wherein there are a plurality of selected substances in said continuously flowing stream, including the step of passing said at least a portion of said stream from said modulator means through a chromatographic column capable of separating said selected substances into a stream through said column in a known manner to said detector means, and wherein said step of comparing includes comparing said produced response signal with said predetermined program controlling said modulator means and said known manner of separating in said chromatographic column to produce a comparison signal identifying variations in said produced signal related to said modulator control, and producing a continuous representation of the presence of said selected substances in accord with said signal identifying variations produced by said comparison.

4. The method of Claim 1, 2 or 3 including the step of passing the output of said modulator means through a preprocessing means for filtering unwanted signals of said stream from further steps of said method.

5. The method of Claim 1, 2 or 3 including the step of introducing a known substance to said continuously flowing stream to produce a response from said comparison step for calibration of said method.

6. The method of Claim 1, 2 or 3 wherein said modulator means comprises one or more modulators controlled in accord with said predetermined manner.

7. The method of Claim 1, 2 or 3 wherein said detector is a detector selected from the group including:
a flame ionization detector;
a thermal conductivity detector;
an electron capture detector;
and a photoionization detector
for producing said response signal.

8. The method of claim 1, 2 or 3 wherein said modulator means is a means selected from the group including:
a thermal modulator;
a catalytic modulator;
a radiation responsive modulator;
and a means for destroying a component of said continuous stream
for producing said modulation of said characteristic of said stream.

9. The method of claim 1, 2 or 3 wherein said control of said modulator means comprises a preprogrammed microprocessor means.

10. The method of Claim 2 wherein said continuously flowing stream is automotive exhaust from an internal combustion engine operating on a fuel mixture of methanol and gasoline and said two different chemical substances are methanol and hydrocarbons, said modulator being a means for chemically modifying the methanol in said portion of said continuously flowing stream passing through said modulator, wherein said controlling of said modulator causes a predetermined chemical modification of said methanol present in said modulator, and said detecting means produces a response signal in accord with said chemical modification, and said correlation representation is an indication of the presence of methanol in said flowing stream.

11. The method of Claim 1, 2 or 3 wherein said predetermined manner of controlling said modulator is a thermal variation of said modulator with said flowing stream present to cause a change in the volume of said one of said two substances passing through said modulator.

12. The method of Claim 2 wherein said continuously flowing stream is a stream containing methanol and hydrocarbons, said stream is divided into two streams with a first portion flowing through a modulator containing a chemical modifying material for methanol then flowing through a first valving means to said detecting means and a second portion flowing through a second valving means directly to said detecting means, said valving means being controlled in said predetermined manner for switching said first and second portions of said stream separately to said detecting means for producing said response signal.

13. An apparatus for quantifying the presence of two different chemical substances in a mixture of at least those two substances in a continuously flowing stream comprising:

a) means for containing at least a portion of said continuously flowing stream;

b) modulating means operating on said contained stream for modulating a characteristic of certain components of said contained stream in a manner to relatively effect a characteristic of at least one of said two different chemical substances with respect to the other of said chemical substances;

c) detecting means operable on said contained stream and responsive to the characteristics of said total contained stream for producing a detection signal representative of the total content of chemical substances in said contained stream;

d) control means for controlling said modulating means in a predetermined manner to modulate a characteristic of said at least one of said two different chemical substances relative to said other chemical substance and to cause modulation said characteristic of said total contained stream in accord with said modulating means relative effect on said two different chemical substances;

e) and means for comparing said detection signal with said predetermined manner of control of said modulating means to identify variations in said detection signal corresponding to said control of said modulating means to quantify the presence of said two different chemical substances in said mixture.

14. The apparatus of Claim 13 wherein the chemical substances to be quantified are methanol and hydrocarbons in a continuous stream of exhaust gases from an engine fueled with a mixture of methanol and hydrocarbon fuels, wherein said modulating means is a means for operating on said continuous stream for modulating a characteristic of said exhaust gases in a manner to relatively effect methanol and hydrocarbons in said stream differently, said detecting means is responsive to said methanol and said hydrocarbons as well as other components of said exhaust gases, and said control means is a means for controlling said modulating means in a predetermined manner to relatively effect methanol and hydrocarbons in said continuous stream differently and to cause modulation of said exhaust gases in accord with said relative effects.

15. The apparatus of Claim 14 including filter means between said modulating means and said detecting means for controlling portions of said exhaust gases which do not represent said methanol and hydrocarbons in said exhaust gases.

16. The apparatus of Claim 13 wherein said modulating means is a means for thermally effecting said portion of said continuous stream to cause said effect on said characteristic of said at least one substance.

17. The apparatus of Claim 13 wherein said modulating means is a means having a catalytic effect on said at least one substance to effect said variation in said characteristic, and said control means controls the passage of said continuous stream through said means having said catalytic effect.

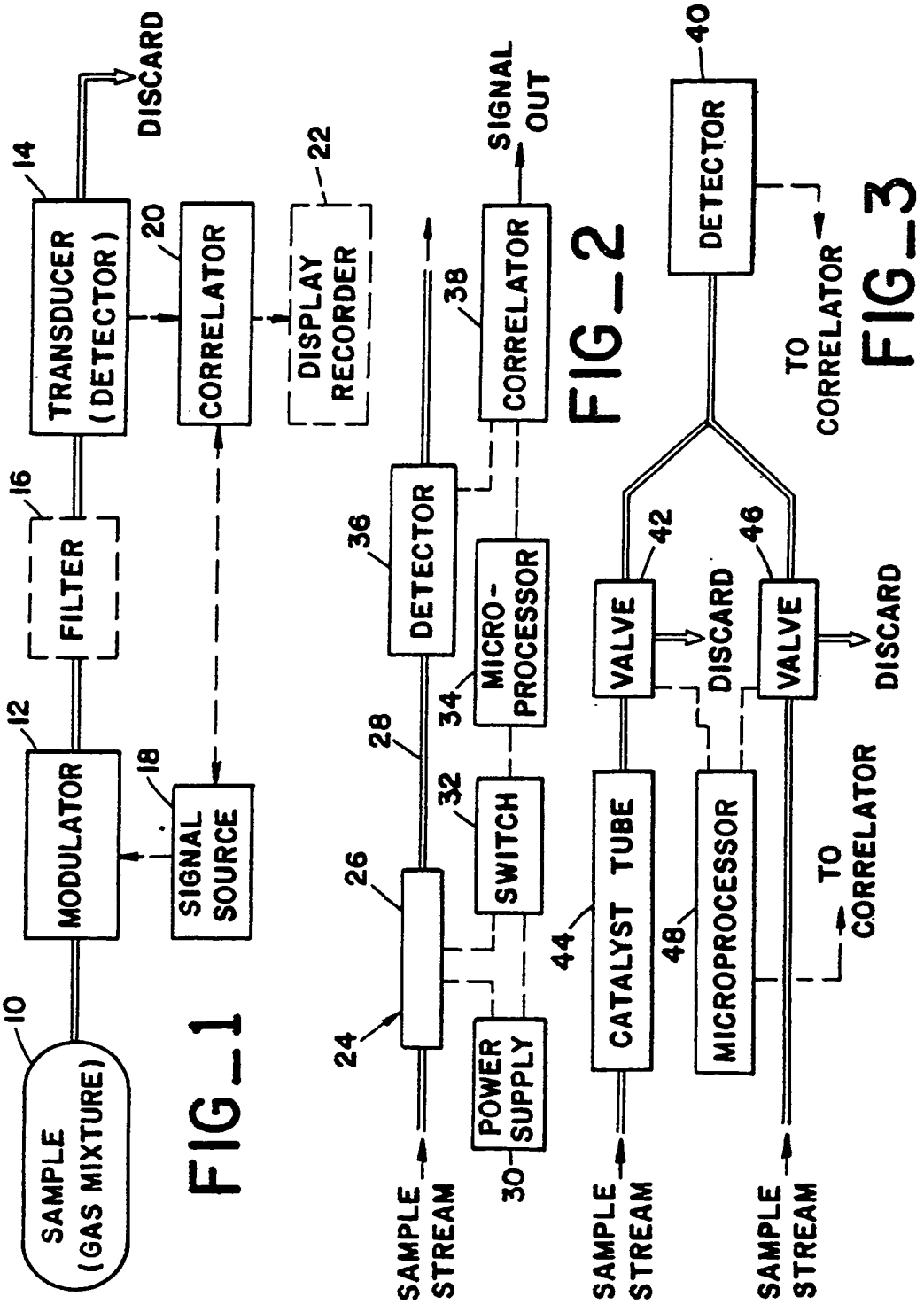
18. The apparatus of Claim 13 wherein said control means and said means for correlating are controlled by a microprocessor.

19. The apparatus of Claim 17 including controlled valving means for controlling said passage of said continuous stream through said means having said catalytic effect and wherein said predetermined control of said modulating means is a control of said controlled valving means.

20. The apparatus of Claim 13 including a source of calibration gases and means for controlling passage of said calibration gases through said apparatus to establish a response function of said apparatus to said substances in said continuous stream.

21. The apparatus of Claim 13 including a filter, a pump, a switching valve, a control valve and a pressure gauge between said continuous stream input and said modulating means, a source of calibration gases connected to said switching valve for calibrating said apparatus, a chromatographic column between said modulating means and said detecting means, thermal barrier means for maintaining temperature control of said modulating means, said chromatographic column and said detecting means, and a control panel including said control means, said means for correlating, and said means for displaying said correlatiion signal.

22. The apparatus of Claim 13 wherein said modulating means includes a granular solid from the class including calcium chloride and cobalt chloride.


SAMPLE (GAS MIXTURE)
10
MODULATOR
12
FILTER
16
TRANSDUCER (DETECTOR)
14
SIGNAL SOURCE
18
CORRELATOR
20
DISCARD
DISPLAY RECORDER
22
FIG_1
SAMPLE STREAM
24
DETECTOR
36
MICRO-PROCESSOR
34
CORRELATOR
38
SIGNAL OUT
SWITCH
32
POWER SUPPLY
30
28
26
FIG_2
DETECTOR
40
TO CORRELATOR
VALVE
42
VALVE
46
DISCARD
DISCARD
CATALYST TUBE
44
MICROPROCESSOR
48
TO CORRELATOR
SAMPLE STREAM
SAMPLE STREAM
FIG_3

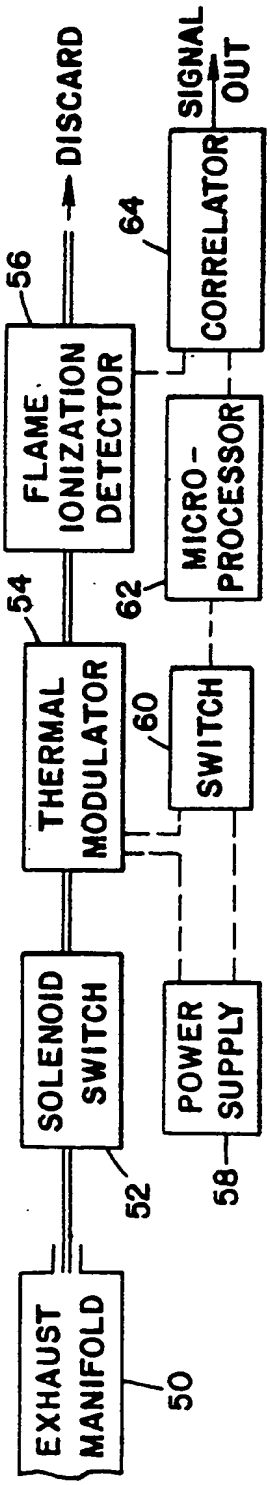

EXHAUST MANIFOLD
50
SOLENOID SWITCH
52
THERMAL MODULATOR
54
FLAME IONIZATION DETECTOR
56
DISCARD
CORRELATOR
64
SIGNAL OUT
MICRO-PROCESSOR
62
SWITCH
60
POWER SUPPLY
58

FIG_4

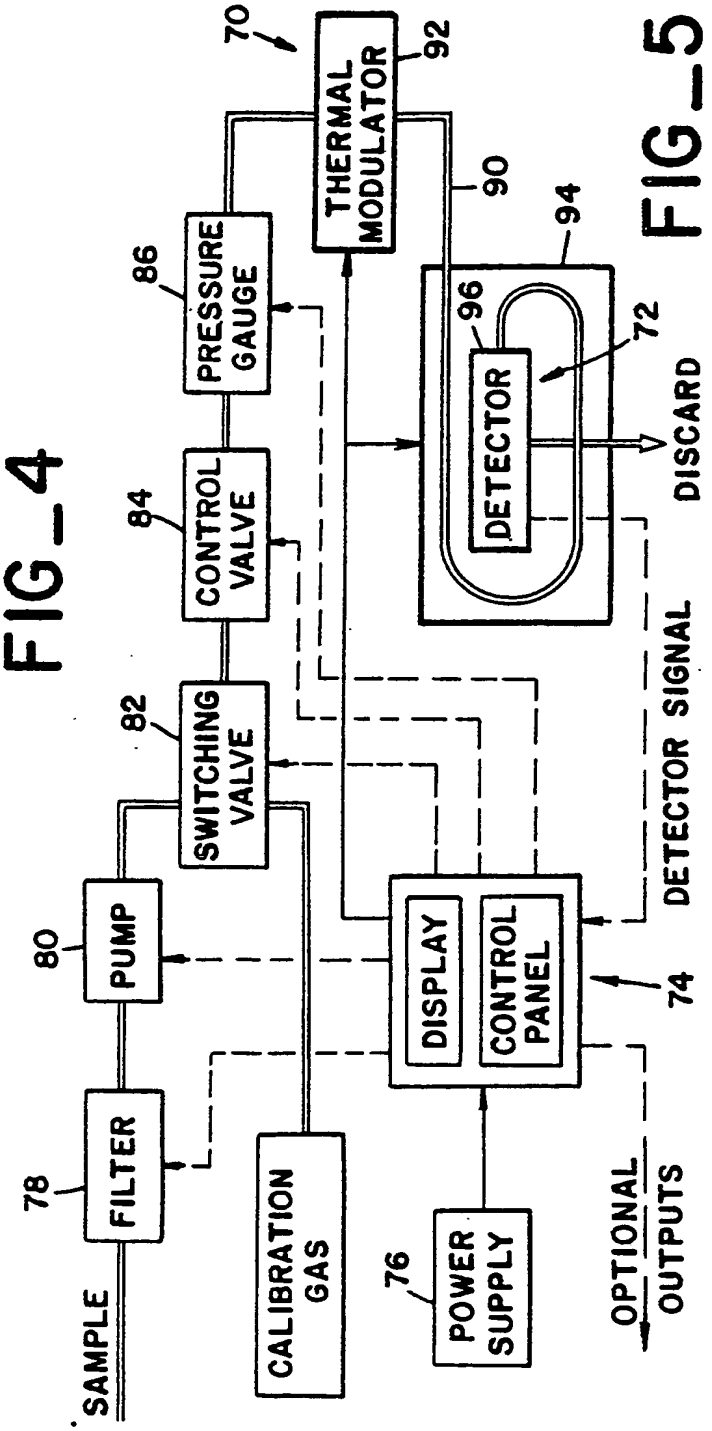

SAMPLE
FILTER
78
PUMP
80
SWITCHING VALVE
82
CONTROL VALVE
84
PRESSURE GAUGE
86
THERMAL MODULATOR
70
92
90
94
DETECTOR
96
72
DISCARD
CALIBRATION GAS
POWER SUPPLY
76
DISPLAY
CONTROL PANEL
74
DETECTOR SIGNAL
OPTIONAL OUTPUTS

FIG_5

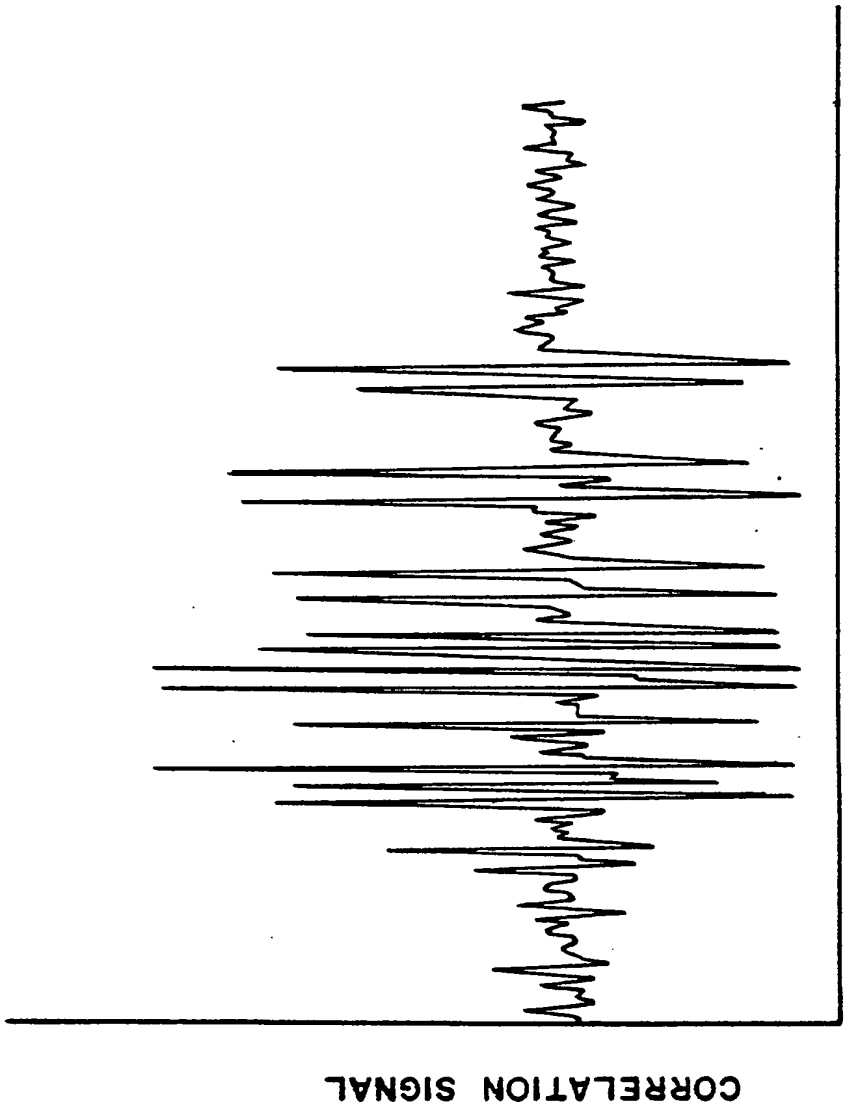



FIG_6

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/US86/01625

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (4): G01N 33/00 U.S. Cl. 436/52

## II. FIELDS SEARCHED

Minimum Documentation Searched [4]

| Classification System | Classification Symbols |
|---|---|
| U.S. | 73/23, 23.1, 25, 27R; 250/281-283; 324/464; 422/54, 81, 83, 89, 92, 93; 436/52, 55, 131, 139-143, 154-159 |

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

## III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

| Category [*] | Citation of Document, [16] with indication, where appropriate, of the relevant passages [17] | Relevant to Claim No. [18] |
|---|---|---|
| X | EP, A, 135,135 (HONEYWELL,INC) 27 MARCH 1985 See the entire document. | 1,2,6,13 |
| X | US, A, 4,120,657 (NAGY ET AL) 17 OCTOBER 1978 See the entire document. | 1,6,9,13,18 |
| Y | US, A, 4,197,177 (PROCTOR) 08 APRIL 1980 See column 3 lines 20-26. | 22 |
| Y | US, A, 3,977,836 (MATSUDA ET AL) 31 AUGUST 1976 See the entire document. | 8,11,12,16,19 |
| Y | US, A, 3,967,933 (ETESS ET AL) 06 JULY 1976 See the entire document. | 6,8,9,12,15,18 19,21 |
| Y | GB, A, 1,243,705 (BOTHE ET AL) 25 AUGUST 1971 See column 1 lines 24-33. | 8 |
| Y | ENVIRONMENTAL SCIENCE & TECHNOLOGY, VOLUME 12, No. 9 issued SEPTEMBER 1970, G. KARELS ET AL, "Continuous Method for Sampling Stack Gases for Total Carbon", See page 1048 | 8,11,12,15,16 19 |

[*] Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

## IV. CERTIFICATION

| Date of the Actual Completion of the International Search [2] | Date of Mailing of this International Search Report [2] |
|---|---|
| 21 OCTOBER 1986 | 24 OCT 1986 |
| International Searching Authority [1] | Signature of Authorized Officer [20] |
| ISA/US | Michael S. Gzybowski |

Form PCT/ISA/210 (second sheet) (May 1986)

International Application No. PCT/US86/01625

III. DOCUMENTS CONSIDERED TO BE RELEVANT (C NTINUED FROM THE SECOND SHEET)

| Category * | Citation of Document, [16] with indication, where appropriate, of the relevant passages [17] | Relevant to Claim No [18] |
|---|---|---|
| A | US, A, 4,019,863 (JENKINS ET AL) 26 APRIL 1977 | |
| A | US, A, 3,753,653 (BRIEVA ET AL) 21 AUGUST 1973 | |
| A | US, A, 3,711,251 (GOODSON ET AL) 16 JANUARY 1973 | |